

# SCIENCE FOR CERAMIC PRODUCTION

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## PHYSICAL AND TECHNOLOGICAL FACTORS DETERMINING Y–ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> COMPOSITE NANOSTRUCTURED CERAMIC DENSITY

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The particulars of the sintering process for Y–ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> ceramic materials with different initial structural modifications (tetragonal or cubic) are studied. The effect of cold isostatic compaction on the volume density of such materials sintered at high-temperature is determined.

**Key words:** composite ceramic, zirconium dioxide, nanosize powder, cold isostatic pressing.

The production of ceramic materials with controllable density and, therefore, porosity is an important technological problem. For ceramic building materials, priority is given to obtaining the maximum density, which determines the high technical properties of such articles. For other applications (filters, catalysts, composites with a porous ceramic matrix, biomaterials) a ceramic with low density but an extended porous structure is needed.

The density of ceramic materials depends on many factors: the particle size of the initial powdered raw material, the conditions of compaction — primarily, the pressing method and pressure, the sintering temperature and time, the presence and properties of different modifying and technological additives, and so forth. The study of the physical mechanisms determining particular technological methods for controlling the density of ceramic materials is a topical problem of materials science, since it permits making a substantiated choice of different technological schemes for obtaining ceramic articles with the required density depending on how the articles are used.

The objective of the present work is to identify the physical processes occurring during technological operations that influence the density of Y–ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> composite ceramic produced from nanopowder with 90 wt.% Y<sub>0.18</sub>Zr<sub>0.82</sub>O<sub>2</sub> and 10 wt.% Al<sub>2</sub>O<sub>3</sub>.

This material is chosen for the following reasons. In the first place, a ceramic composite consisting of zirconium di-

oxide and aluminum oxide is a promising building material. Ceramics made from pure aluminum oxide possesses high mechanical strength and hardness but it is characterized by low toughness, while zirconium ceramics possess high mechanical strength and toughness but low hardness. ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> ceramic composites make it possible to realize simultaneously an entire complex of high mechanical properties which cannot be obtained in the individual components of a composite.

In the second place, yttrium ions are introduced into the ZrO<sub>2</sub> crystal lattice in order to stabilize the required cubic or tetragonal structure (it is well known [1] that zirconium dioxide has three structural modifications — monoclinic, tetragonal, and cubic; in addition, on heating ZrO<sub>2</sub> initially in the monoclinic modification undergoes a polymorphic transformation into the tetragonal phase, which is accompanied by a substantial change in volume and, in consequence, by fracture, which is one of the main drawbacks of zirconium dioxide; for this reason, an important problem is to produce ZrO<sub>2</sub> in the tetragonal or cubic modification, stable in a high temperature interval).

In the experimental system Y–ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> we used a high content (by weight) of the stabilizer (18% yttrium), much higher than that conventionally used only to stabilize the required crystal structure of ZrO<sub>2</sub> (as a rule, ≤ 10% stabilizer). Such a high stabilizer content was necessary to purposefully degrade the sintering of the composite ceramics in this system and thereby gain the possibility of studying the effect of other factors on the density of the material obtained (it is well known [2] that the higher the degree of stabilization of ZrO<sub>2</sub>, the worse its sinterability is).

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In addition, it is desirable to use as the initial material nanopowder containing 90% Y<sub>0.18</sub>Zr<sub>0.82</sub>O<sub>2</sub> and 10% Al<sub>2</sub>O<sub>3</sub> both to optimize the technological process of obtaining the ceramic, related with the decrease of the sintering temperature as a result of rapid diffusion of the sintered nanosize powder, and to improve the properties of the finished ceramic article as a result of the formation of a fine submicron structure of the ceramic during sintering at low temperature.

Chemical precipitation from a 1 : 5 water–isopropanol solution was used to synthesize the initial composition indicated above. This method was chosen because agglomeration and growth of the synthesized nanoparticles are much less likely to occur, making it possible to obtain less agglomerated, smaller particles [3].

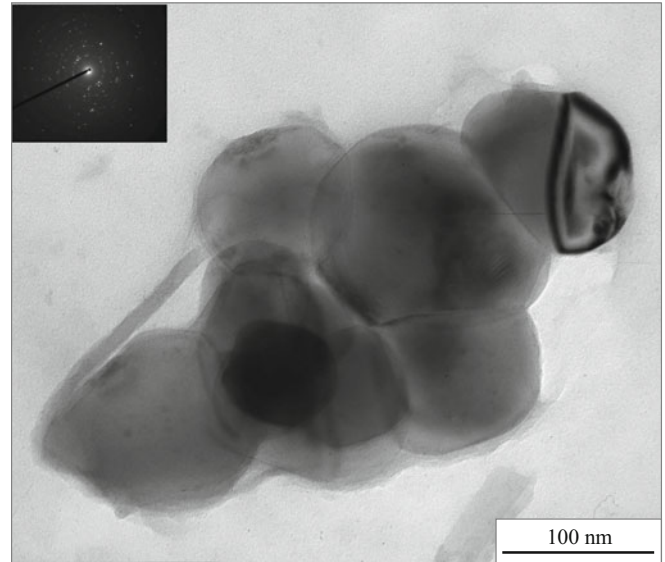
The initial reagents were ZrO(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, and Y(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O; the principal reagent was a water solution of ammonia. The concentration of the salt and precipitator solutions was 0.1 M. The feed rate of the salt solutions was chosen so that the pH would be about 9.5 throughout the entire precipitation process, which was conducted with vigorous mixing. Next, the hydrogel obtained was washed with water and alcohol and dried in air at 50°C for 48 h. At the final stage of synthesis the dried hydrogel (xerogel) was heat-treated in air at high temperature 1200°C for 20 min. This stage of synthesis is necessary in order for the final crystalline structure of the powder to form. Cold isostatic pressing (EPSI 400-200\* 1000Y press) was used to compact the synthesized powder.

A JEM-2100 transmission electron microscope was used to determine the size of the particles of the synthesized powder. A Rigaku Ultima IV diffractometer (CuK<sub>α</sub> radiation, Ni filter) was used to study the phase composition of the synthesized material. The sintering of the ceramic was studied by the dilatometric method using a NETZSCH DIL 402 C dilatometer. The volume density of the sintered ceramic samples was determined by the pycnometric method using an AccuPyc 1340 helium pycnometer.

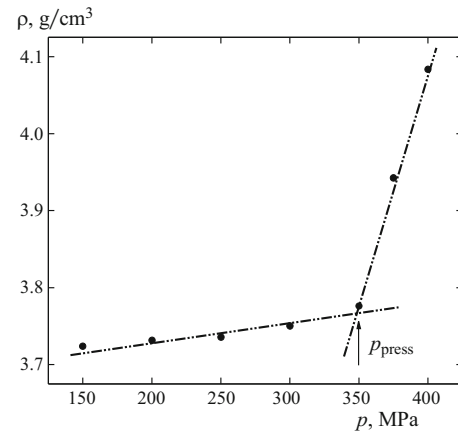
X-ray phase analysis (XPA) of the synthesized powder established that the powder consists of two phases: the main, tetragonal phase with the *P42/nmc* space group symmetry characteristic for zirconium dioxide and an additional trigonal phase with *R3c* space group symmetry characteristic for corundum Al<sub>2</sub>O<sub>3</sub>.

The TEM studies showed that the powder consists of spherical particles of average size 50 – 100 nm (Fig. 1).

The following values of the isostatic pressures *p* were used to compact the nanosize powder with the composition presented above: 150, 200, 250, 300, 350, 375, and 400 MPa. The dependence of the volume density  $\tilde{n}$  of the compacted samples on the pressing pressure *p* is displayed in Fig. 2: there are two rectilinear sections. Below  $p_{\text{press}} = 350$  MPa, as pressure increases, the density of the samples increases very little at the average rate about  $2.58 \times 10^{-4}$  (g/cm<sup>3</sup>)/MPa; above  $p_{\text{press}}$  the density  $\tilde{n}$  starts to increase rapidly at the average rate about  $5.97 \times 10^{-3}$  (g/cm<sup>3</sup>)/MPa.



**Fig. 1.** TEM image of particles of synthesized powder consisting of 90% Y<sub>0.18</sub>Zr<sub>0.82</sub>O<sub>2</sub> and 10% Al<sub>2</sub>O<sub>3</sub>.



**Fig. 2.** Volume density  $\rho$  of compacts versus the compaction pressure *p*.

It is helpful to compare the experimental values of the density of the compacted samples with the theoretical density of material with the composition 90% Y<sub>0.18</sub>Zr<sub>0.82</sub>O<sub>2</sub> and 10% Al<sub>2</sub>O<sub>3</sub>. The theoretical density can be evaluated from the formula

$$\rho_{\text{th}} = 0.9\rho_1 + 0.1\rho_2, \quad (1)$$

where  $\rho_1 = 6.10$  g/cm<sup>3</sup> is the density of zirconium dioxide in the tetragonal modification and  $\rho_2 = 3.99$  g/cm<sup>3</sup> is the density of aluminum oxide in the trigonal modification.

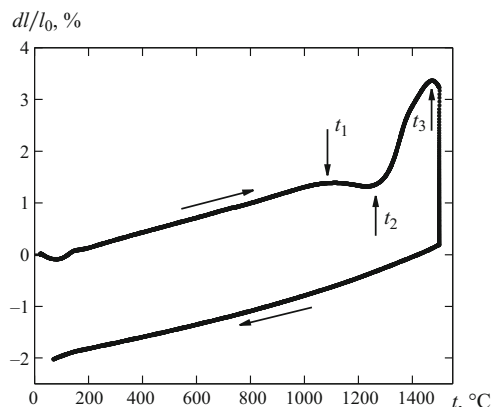
The density  $\rho_{\text{th}}$  calculated from the relation (1) is 5.889 g/cm<sup>3</sup>. Thus, the density of the compacted material is much lower than the theoretical value, equal to 63.23% (for pressure 150 MPa), 63.36% (200 MPa), 63.43% (250 MPa),

63.68% (300 MPa), 64.13% (350 MPa), 66.94% (375 MPa), and 69.34% (400 MPa) of the theoretical density.

Next, the samples compacted under different cold isostatic compaction pressures were heat-treated at high temperature in order to study the sintering process. At the first stage of heat-treatment the samples compacted under different pressures were heated from room temperature to 1500°C in 5 h, soaked at this temperature for 2 h, and then cooled to room temperature in 5 h. This treatment was conducted in the chamber of a dilatometer with an atmosphere with the composition (by weight) 80% nitrogen and 20% oxygen. It was determined that for all samples the linear dimensions change during the treatment process identically and are practically independent of the compaction pressure. As an example, the results of the dilatometric analysis for a sample compacted under pressure 150 MPa are displayed in Fig. 3. It is evident from the figure that on heating from room temperature to  $t_1 \approx 1085^\circ\text{C}$  the sample stretches at a constant rate, so that the elongation at temperature  $t_1$  is of the order of 1.41% of the initial length  $l_0$ . Above  $t_1$  the length of the sample starts to decrease with increasing temperature, which could attest to sintering onset. However, at the temperature  $t_2 \approx 1245^\circ\text{C}$ , where the shrinkage of the sample is 1.31%, the sample once again starts to stretch but at a higher rate than below the temperature  $t_2$ . So, in the temperature interval from  $t_1$  to  $t_3 \approx 1470^\circ\text{C}$  the change of length  $dl/l_0$  ranges from 1.31 to 3.36%. The sintering process restarts at the temperature  $t_3$ . With isothermal soaking at  $1500^\circ\text{C}$  the maximum shrinkage  $(dl/l_0)_{\text{max}}$  reaches 2% of the initial size of the sample. When the sample is subsequently cooled to room temperature its length decreases monotonically without any of the anomalous changes observed at temperature  $t_2$  during heating.

Thus, the dilatometric analysis shows that the dimensional change of the experimental sample is quite complex and consists of several stages. The characteristic temperatures  $t_1$ ,  $t_2$ , and  $t_3$  as well as the maximum shrinkage  $(dl/l_0)_{\text{max}}$  are independent of the pressure used for isostatic compaction of the samples and are the same as those determined for the sample compacted under pressure 150 MPa. It was also found that the density of each sample after heat-treatment at high temperature increases approximately by the same amount about 3.5% of the initial value.

The anomalous change of the length of a sample in Fig. 3 under heating could be due to a structural phase transition. It is known [4] that on heating above  $2300^\circ\text{C}$  the coarse-crystalline tetragonal modification of zirconium dioxide transforms into the cubic modification. As the grain size decreases to several tens of nanometers, a large decrease of the onset temperature for the formation of the cubic modification of zirconium dioxide occurs right up to temperature about  $1100^\circ\text{C}$ . Because nanosize powder was employed in the present study it is logical to suppose that the anomalous size change of the specimen occurring at  $t_2$  could be due to a structural phase transition from the tetragonal into the cubic



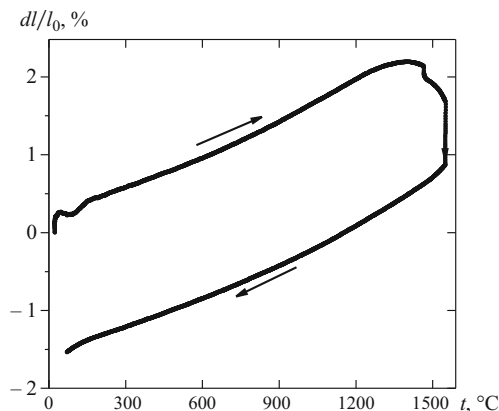
**Fig. 3.** Dilatometric analysis of a sample compacted at pressure 150 MPa with heating (top curve) to temperature  $1500^\circ\text{C}$ , isothermal soaking at this temperature, and subsequent cooling (bottom curve).

modification, which is stable and remains during isothermal soaking at  $1500^\circ\text{C}$  as well as during subsequent cooling to room temperature.

To check this supposition, after heat-treatment at high temperature the samples were subjected to XPA. Indeed, it was found that the characteristic reflections of cubic zirconium dioxide with space group  $Fm\bar{3}m$  (instead of the tetragonal  $P42/nmc$  phase which exists before high-temperature treatment) are present in the diffraction pattern of the sample compacted under pressure 150 MPa and after high-temperature heat-treatment at  $1500^\circ\text{C}$ . A second phase — trigonal corundum  $\text{Al}_2\text{O}_3$  with space symmetry group  $R\bar{3}c$  — also remains in the sample. We note that the presence of two different phases in the experimental ceramic material is precisely characteristic for a composite ceramic.

Therefore, high-temperature heat-treatment of the sample at  $1500^\circ\text{C}$  does indeed result in a transition of the initial tetragonal modification of zirconium dioxide into the cubic modification.

Evidently, when the cubic modification is heated in a temperature interval that includes the temperature  $t_2$  no anomalies associated with the structural phase transition tetragonal phase  $\rightarrow$  cubic phase should be observed. Such behavior was indeed observed in the experiment. The results of a dilatometric study of a sample compacted under pressure 150 MPa and after heat treatment at  $1500^\circ\text{C}$  and therefore having a cubic structure at room temperature are presented in Fig. 4. In this case, the sample was heated to  $1550^\circ\text{C}$  in air, isothermally soaked at this temperature for 30 min, and then cooled to room temperature. The change of the length of the sample initially in the cubic modification, presented in Fig. 4, differs considerably from the behavior of the sample initially in the tetragonal modification (Fig. 3). The sample in the cubic modification stretches monotonically with increasing temperature; sintering starts at temperature of the order of  $1300^\circ\text{C}$  and is accompanied by shrinkage of the sample as it is heated to  $1550^\circ\text{C}$  as well as with isothermal

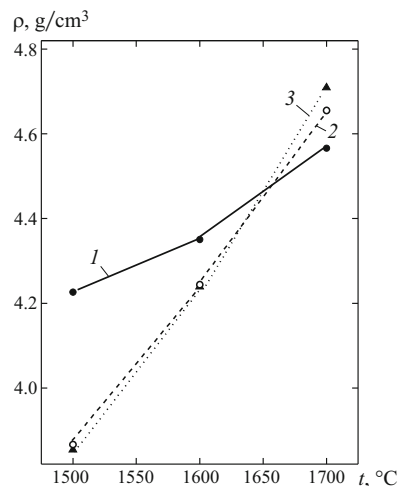


**Fig. 4.** Dilatometric analysis of a sample containing 90% Y<sub>0.18</sub>Zr<sub>0.82</sub>O<sub>2</sub> and 10% Al<sub>2</sub>O<sub>3</sub> with cubic initial structure, compacted under pressure 150 MPa with heating (top curve) to temperature 1550°C, isothermal soaking at this temperature, and subsequent cooling (bottom curve).

soaking at this temperature. During subsequent cooling the dimensions of the sample decrease monotonically, so that the maximum shrinkage is about 1.5% of the initial length.

Thus, it can be concluded from dilatometric and x-ray phase analyses that when heated above  $t_2 \approx 1245^\circ\text{C}$  the experimental samples initially in the tetragonal modification undergo a structural phase transition, which is accompanied by a change of symmetry  $P42/nmc \rightarrow Fm\bar{3}m$  and impedes compaction of the ceramic during sintering.

Heat-treatment was conducted for 1 h at 1600°C and 2 h at 1700°C. In both cases the treatment was performed in air. The dependences of the density of the samples compacted under pressures 150, 250, and 400 MPa on the heat-treatment temperature (1500, 1600, and 1700°C) are presented in Fig. 5. It can be concluded on the basis of the data presented in Fig. 5 that decompaction occurs in the experimental system, i.e., after the second high-temperature anneal the density of the samples compacted under lower isostatic pressing pressure and having a lower initial volume density is higher than the density of the samples which are denser in the initial state. So, the density of the sample compacted under pressure 150 MPa was 4.709 g/cm<sup>3</sup> (the initial value after compaction 3.7235 g/cm<sup>3</sup>), 4.655 g/cm<sup>3</sup> under 250 MPa (the initial value after compaction 3.7354 g/cm<sup>3</sup>), and 4.566 g/cm<sup>3</sup> under 400 MPa (the initial value after compaction 4.0833 g/cm<sup>3</sup>). According to [2], the phenomenon of decompaction could be associated with the appearance and development of a system of cracks during sintering of the ceramic samples compacted under high pressures.



**Fig. 5.** Variation of the density of a YZrA ceramic sample versus the temperature of high-temperature heat-treatment: 1) compaction pressure 400 MPa; 2) 250 MPa; 3) 150 MPa.

In summary, the samples compacted under low pressures 150 and 250 MPa (on the section to  $p_{\text{press}} = 350$  MPa, see Fig. 2) exhibit better sinterability than the sample compacted under the maximum pressure 400 MPa, since the density of the samples compacted under pressures 150 and 250 MPa depends more strongly on the temperature of high-temperature treatment.

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